UNIVERSITEIT VAN PRETORIA
UNIVERSITY OF PRETORIA
YUNIBESITHI YA PRETORIA

University of Pretoria

Fatty acid intercalated layered double hydroxides as additives for Jojoba oil and polymer matrices

by

Lumbidzani Moyo

Submitted in partial fulfilment of the requirements for the degree of

Philosophiae Doctor in Chemical Technology

in the

FACULTY OF ENGINEERING, BUILT ENVIRONMENT AND
INFORMATION TECHNOLOGY,
UNIVERSITY OF PRETORIA

Pretoria

November 2012

Declaration

I, Lumbidzani Moyo, the undersigned, declare that the thesis that I hereby submit for the degree PhD in Chemical Technology at the University of Pretoria is my own work, and has not previously been submitted by me for degree purposes or examination at this or any other university.

Pretoria, November 2012

…………………………….
Lumbidzani Moyo

Fatty acid intercalated layered double hydroxides as additives for Jojoba oil and polymer matrices

Student: Lumbidzani Moyo

Supervisor: Prof. Walter W. Focke

Co-supervisor: Dr. Frederick J. W. Labuschagne

Department: Chemical Engineering

University: University of Pretoria

Degree: PhD (Chemical Technology)

Synopsis

Fatty acid intercalated layered double hydroxides were used as additives for Jojoba oil and polymer matrices. The first phase of the study was to intercalate carboxylic acids (C_{14} to C_{22}). These were successfully intercalated into layered double hydroxides (LDHs), with the formula $[Mg_{0.7}Al_{0.3}(OH)_2](CO_3)_{0.15}\cdot 0.5H_2O$. The one-pot synthesis consistently yielded a bilayer intercalated product for the range of acids employed. The intercalated anions had an orientation tilt angle of 55–63°, depending on the length of the fatty acid chain. However, there is an indication that the anion exchange process employed in this study is accompanied by probable dissolution and recrystallisation of the LDH. This is supported by the different growth habits and sizes of platelets observed through scanning electron microscopy (SEM). Moreover, the organo-LDH platelets were found to have varying M^{II}/M^{III} compositions, ranging from 1.65 to 6, indicating that the one-pot synthesis yields an array of mixed metal hydroxides.

Polymer composites, containing 5% and 10 wt.% of stearate intercalated layered double hydroxides (LDH-stearate) and neat layered double hydroxides (LDH-CO_3), were prepared via melt-compounding to explore the use of LDHs as an additive. The stearate modified starting material was bilayer-intercalated clay. During melt compounding, excess stearates were released and the clay reverted to a monolayer-intercalated form. Comprehensive characterisation and study of the fatty acid-intercalated LDH showed that these organoclay hybrids exhibit thermotropic behaviour. This behaviour ultimately leads to the exudation of excess fatty acid. The exuded stearates were found to have lubricating and plasticising effects on the poly(ethylene-co-vinyl acetate) (EVA) and linear low density polyethylene (LLDPE) matrices. Strong hydrogen bond interactions between the chains of poly(ethylene-co-vinyl alcohol) (EVAL) and the clay platelet surfaces overwhelmed the lubrication effect and caused an increase in the melt viscosity of this matrix. The notched Charpy impact strength of this composite was almost double that of the neat polymer. It appears that this can be attributed to the ability of the highly dispersed and randomly oriented nanosized clay platelets to promote extensive internal microcavitation during impact loading. The creation of a large internal surface area provided the requisite energy dissipation mechanism.

The study also considered fatty acid-intercalated LDH as an argillaceous mineral for potential use as a rheological additive in Jojoba oil. A minimum of 20 wt.% LDH in Jojoba oil formulation was found to be stable, i.e. it did not form separate layers on standing. The viscosity of the neat Jojoba oil demonstrated Newtonian behaviour, whereas the modified LDH/Jojoba oil formulation shear thinned, which is a typical non-Newtonian behaviour. Viscosity as a function of temperature showed complex rheological behaviour for the long chain fatty acids C_{16} to C_{22}. The viscosity increase is assumed to be due to a combination of three events, which include the formation and changes of LDH microstructures within the oil, the loss of excess fatty acids into the oil matrix, and the formation of fatty acid crystal networks. Shear action also induced some delamination of the clay platelets.

Keywords: Layered double hydroxides, Intercalation, Fatty acid, Nanocomposites, Thickener

Acknowledgements

The author would like to extend her sincere gratitude to:

- The Lord Almighty, my El Shaddai, for His blessings and the grace that He has abundantly bestowed on me.
- Prof. Walter W. Focke for his guidance and support, as well as the contributions and encouragement that he gave me throughout the course of this work.
- My co-supervisor Dr Johan Labuschagne for the discussions as we tried to understand and explain the numerous results obtained.
- Bervelie Davies and Lynn O'Niell for taking time to read and edit my thesis.
- Wiebke Grote (XRD), Chris van der Merwe, Alan Hall (TEM), Andre Botha (SEM) and Onius Sitando (ICP-OES).
- My colleagues at the Institute of Applied Materials, University of Pretoria, Pedro Massinga Jr, Hermínio Muiambo, Nontete Nhlapo, Shephard Tichapondwa, Washington Mhike, Mthokozisi Sibanda, Shatish Ramjee and Hendrik Oosthuizen, for their unending support and companionship.
- Terence and Naardirah who assisted in carrying out some of the experimental work.
- My parents Anderson and Ethel – thank you for your unwavering support, I could have not asked for a better pair. I'm truly blessed. To my brothers Busisa, Zwelithini, Loius and Andy – thank you for the encouragement. I am what I am because of you. Percy – thank you for the insightful discussions.
- Last but not least, I would like to thank my husband Mthulisi Nxumalo, for his patience and understanding during the course of my studies.

Preface

The central theme of the study was to explore the nature and properties of fatty acid modified layered double hydroxides (LDHs) and their potential use as additives in polymer matrices and Jojoba oil. The first phase of the project involved intercalating long chain fatty acids, i.e. from C_{14} to C_{22}, and fully characterising the modified LDH. The stearic acid (C_{18}) intercalant was ultimately chosen due to its abundance and availability, its substantially long chain length and its reproducibility during the intercalation trials for the implementation of the stages that followed. The second and third phases entailed the use of stearate modified LDH (LDH-stearate) in the preparation of polymer composites and as an additive in Jojoba oil. The thesis is so structured that these three different phases of the study are presented in self-contained chapters (i.e. Chapters 2–4). The highlight of the work is the improvement of the mechanical properties of LDH-based polymer nanocomposites. LDHs offer an alternative to natural clay minerals such as smectites, which have been traditionally used in clay nanocomposites.

The thesis comprises five chapters, each with its own list of references, and appendices:

Chapter 1 is an introduction to the study, with a brief overview of the nature and history of layered double hydroxides (LDHs) and of the two main areas under review in this study, i.e. LDH-based polymer composites and the possible use of LDHs as argillaceous material in Jojoba oil.

Chapter 2 examines the nature, structure, formulae and preparation techniques for LDHs. It further introduces the reader to intercalation, modification methods and the orientation of intercalated fatty acids. It also gives comprehensive details of the intercalation procedure used and the characterisation of the fatty acid-intercalated LDHs used in this study.

Chapter 3 defines polymer composites and distinguishes nanocomposites from conventional composites. It looks into the different preparation techniques for LDH-based polymer composites. The chapter also reviews the properties observed in the resultant composites. It presents a full characterisation of the LDH-based polymer composites of three different polymer matrices. The composites obtained were fully characterised with regard to the type of composite, thermal stability, mechanical properties and viscoelastic behaviour.

Chapter 4 examines the anomalous thickening mechanism of LDH-stearate in Jojoba oil as a function of temperature. A brief overview of the colloidal dispersions of LDHs in different media, i.e. aqueous, non-aqueous and emulsions is given.

Chapter 5 summarises the study and the key findings. As the concluding chapter, it provides recommendations on future research in the field and other possible applications of LDHs.

The **References** provide a record of the literature consulted in the course of this study, which was also used to elucidate the findings of the study.

The **Appendices** contain complementary and supplementary data generated during the study; these are divided according to the corresponding chapters.

TABLE OF CONTENTS

List of Figures

List of Tables

List of Acronyms, Abbreviations and Definitions

AEC	Anionic exchange capacity – Amount of exchangeable anions available with the crystal structure of an adsorbent material, expressed in meq/100 g
AFM	Atomic force microscopy
DMA	Dynamic mechanical analysis/analyser
DSC	Differential scanning calorimetry
EDS	Energy dispersive X-ray spectroscopy
EVA	Ethylene vinyl acetate
EVAL	Ethylene vinyl alcohol
FTIR	Fourier transform infrared
HT	Hydrotalcite
ICP-OES	Inductively coupled plasma optical emission
LDH	Layered double hydroxides
LDH-Be	LDH-behenate
LDH-My	LDH-myristate
LDH-Pa	LDH-palmitate
LDH-St	LDH-stearate
LDO	Layered double oxide
LLDPE	Linear low-density polyethylene
MFI	Melt flow index
PE	Polyethylene
PLLA	Poly(L-lactide)
PMMA	Polymethyl methacrylate
POM	Polarised optical microscopy
PP	Polypropylene
PS	Polystyrene
SDS	Sodium dodecyl sulphate
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TG(A)	Thermogravimetry (Thermogravimetric analysis)
UV	Ultraviolet
XRD	X-ray diffraction

Definitions

Anhedral	Refers to poorly formed crystal with no distinct faces
Delamination	A process in which layers of a multi-layered structure separate
Exfoliation	A process in which layers of a multi-layered structure are separated into single sheets
Fatty acid	Carboxylic acid, is an organic compound with a –COOH functional group
Intercalation	A process in which atoms, ions or molecules are inserted between the layers of a two-dimensional crystal lattice host
Organo-LDH	Surfactant/fatty acid modified layered double hydroxides
Peptisation	To disperse a suspension to form a colloid
Subhedral	Moderately formed crystals
Thermotropic	Changes in structure as temperature changes
Euhedral	Fully-faced crystals, well-formed with sharp, easily recognisable crystal faces.